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SOME RESULTS OF A DETERMINATION OF THE CONCENTRATION OF SULFUR DIOXIDE IN THE FREE ATMOSPHERE [Nekotoryye rezul'taty opredeleniya kontsentratsii sernistogo gaza v svobodnoy atmosfere]

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SOME RESULTS OF A DETERMINATION OF THE CONCENTRATION OF SULFUR DIOXIDE IN THE FREE ATMOSPHERE

O.P. Petrenchuk and V.M. Drozdova

The gaseous compounds of sulfur play an important role in the pollution of atmospheric air. The most widespread pollutant in the troposphere is sulfur dioxide, which is produced primarily as the result of combustion of fuel oil. However, research conducted by a number of authors [6, 8, 9] indicates that sulfur compounds, both in gaseous and aerosol form, occur everywhere in the stratosphere as well as in the troposphere.

Interest in studying sulfur compounds in the atmosphere has increased markedly during recent times in conjunction with the discovery of the so-called sulfate layer, composed of sulfate particles, at an altitude of 20-25 km in the stratosphere [8-10]. Various opinions exist with regard to its origin. C. Junge and a number of other authors [8, 9] explain the existence of this layer by the oxidative processes of gaseous compounds of sulfur, primarily sulfur dioxide and hydrogen sulfide, and photochemical reactions in which they participate. It is considered that the above-mentioned compounds of sulfur are tropospheric in origin. Martell [10] states that the boundaries of this layer are less clear, and suggests that it is caused primarily by the coagulation of Aitken nuclei which consist primarily of sulfates at high altitudes. However, the lack of experimental data on the vertical distribution of sulfur dioxide in the atmosphere prevents us from estimating the relative role of its oxidation or the coagulation of the Aitken nuclei in the formation of the sulfate layer in the lower stratosphere.

The water in clouds, fogs, and precipitation always contains sulfates which frequently constitute the predominant pollutant [1, 4, 5, 9]. On the basis of experimental research which has been conducted [7, 8], it has been suggested that one of the important sources of sulfates in atmospheric water is oxidation of sulfur dioxide in the drops in the presence of catalysts. Consequently, when studying formation of the chemical composition of precipitation, it is important to know the content of the sulfur dioxide in the free atmosphere. However, such data are very sparse at the present time [6].

In view of this, during March and April, 1969, we carried out aircraft measurements of the sulfur dioxide content in the free atmosphere in the vicinity of one of the cities in the northwestern part of the European territory of the Soviet Union. The flights were conducted using a IL-14 aircraft under various meteorological conditions. During the period indicated, a total of 15 flights were made, and 15 vertical profiles of the sulfur dioxide content in the atmosphere up to an altitude of approximately ∠500 meters were obtained.

To measure the concentration of sulfur dioxide, we used the method of West and Gaeke as the most sensitive of the methods usually employed; this method makes it possible to determine the concentration of sulfur dioxide in the solution being analyzed with an accuracy up to 0.1 microgram [11, 2]. The analytical method of West and Gaeke enjoys a considerable advantage in comparison to other methods, in the fact that when it is used it is the gas itself which is trapped, and the presence of sulfate aerosols in the atmosphere has no effect. This method is based on the fixation of sulfur dioxide during the passage of air through a 0.1 N solution of mercuric chloride and sodium chloride $Na_2(HCl_4)$ and the formation of a stable nonvolatile ion of mercury disulfite.

The air samples were collected by means of a TRU-4 rotating apparatus. The air to be studied was aspirated at a rate of 5 liters per minute for 15 to 20 minutes through a U-shaped absorber with a porous membrane filled with 5 ml of absorbent solution. As special studies showed [6], the maximum

possible error in collecting the sample, due to the fluctuations in the rate of air flow during collection of the sample, the losses of the absorbent solution due to spraying and evaporation, the adsorption of traces of gas in the collecting units and the influence of temperature, amounts to approximately ± 10%.

Following selection of the samples during the analysis in the laboratory, special attention was devoted to ensuring that the volume of the absorbent solution, which could decrease as a result of spraying, remained constant at all times and equal to the original amount. This was achieved by adding additional amounts of absorbent solution prior to analysis. The analysis itself was performed by the colorimetric method using pararozanilin hydrochloride and formaldehyde. The final reaction product of this method is the formation of a purple, quite stable substance known as pararozanilin sulfonic acid. The calibration curve was plotted by using freshly prepared working solutions containing 20 and 2 micrograms per milliliter of SO_2, respectively. The sulfur dioxide content in the original solution from which the working solutions were prepared was determined by titration with a 0.01 N iodine solution in addition to the weighed amount. As the indicator in the titration, we employed benzene which is a more sensitive indicator than starch [3]. All of the solutions used were prepared from a freshly obtained bidistillate.

Prior to colorimetry, 0.5 ml of solution of pararozanilin and 0.5 ml of 0.2% formadehyde solution were added to the test tubes containing the samples, after which they were carefully sealed. After 25 minutes had elapsed, a reddish violet color appeared in them and lasted about 30 minutes. Determination of the optical density of the solutions was performed used the FEK-M photocolorimeter in cuvettes having a distance of 10 mm between the working boundaries and using a green light filter.

All of the determinations of the sulfur dioxide content were performed no more than 1 to 3 days following collection of the samples, although, as a preliminary set of laboratory experiments revealed, the samples were stable for up to 8 days. When this period had elapsed, there was a significant

decrease in the concentration of sulfur dioxide, and by the twelth day following the beginning of storage this decrease could amount to 25 to 40% of the initial value as a function of the latter.

During the flights, beginning on approximately 15 March, the entire European territory of the Soviet Union was covered by an extensive low-gradient high-pressure area which lasted until the end of the month. The weather in the northwestern part of the European territory of the Soviet Union was characterized by very gentle winds and a lack of clouds. Industrial smoke hung over the city for many days. On 31 March 1969, the baric field began to change. An extensive deep cyclone formed over Scandinavia. The northwestern part of the European territory of the Soviet Union, including the area where the flights took place, was in a zone of clearly pronounced directional transport from the southwest.

On the days of the flights, immediately before takeoff, air samples were collected on the ground at the air field; during the flights, they were collected at altitudes of 300, 600, 900 and 1200 meters and in some cases at still higher altitudes (all the way to 2600 meters). At these levels, the plane flew around the city in a circle whose radius was approximately 15-20 km. Approximately 20 minutes were consumed in collecting one sample. When the flights were over, the samples were sent to the chemical laboratory for analysis.

The results that were obtained in measuring the concentration of sulfur dioxide in the atmosphere in accordance with the synoptic situation which was observed can be divided into two groups. The first contains all instances of measurement conducted in an anticyclonic situation, characterized by stability, gentle winds, and the existence of temperature inversions. The second group contains data which were obtained under conditions of clearly pronounced transport of air masses with considerable development of turbulence in the atmosphere. Figures 1 and 2 show the results of the measurements of the sulfur dioxide concentration which are typical of the groups mentioned above.

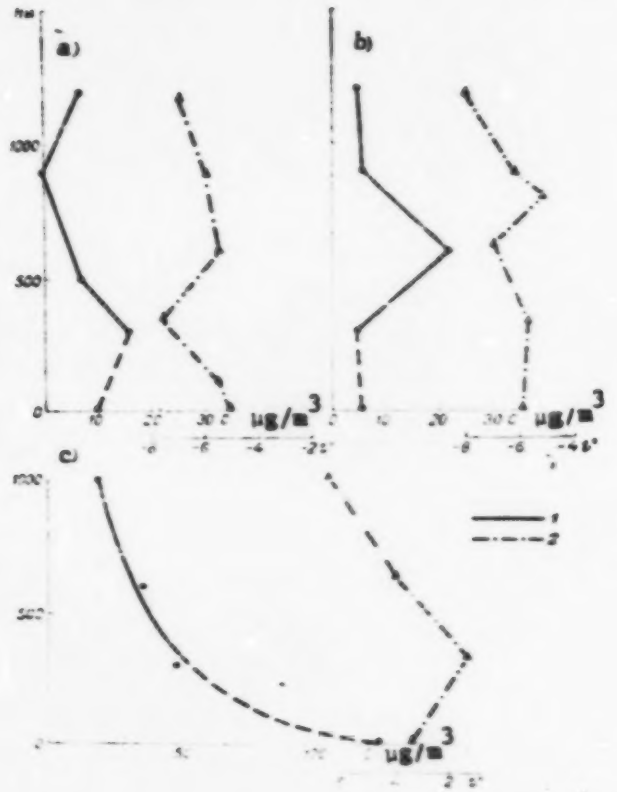

Figure 1. Change in Concentration of Sulfur Dioxide and Air Temperature with Altitude Under Anticyclonic Conditions in March of 1969.

a- 24 March, b- 26 March; c- 19 March; 1- Sulfur dioxide; 2- Temperature.

As we can see from Figures 1 a, and b, a characteristic feature of distribution of sulfur dioxide in the atmosphere under anticyclonic conditions is a marked increase in its concentration in the subinversion layer. At the same time that there is a peak in the concentration of sulfur dioxide, one can also see an altitudinal temperature inversion. It should be pointed out that during the flights there was visual observation of industrial haze and plumes of smoke which extended up to the altitude of the inversion and spread out beneath it. It was under these conditions that we noted the maximum concentration of sulfur dioxide. On the ground, in the vicinity of the air field, the concentration of sulfur dioxide was usually low (approximately 10 micrograms/m^3, but in

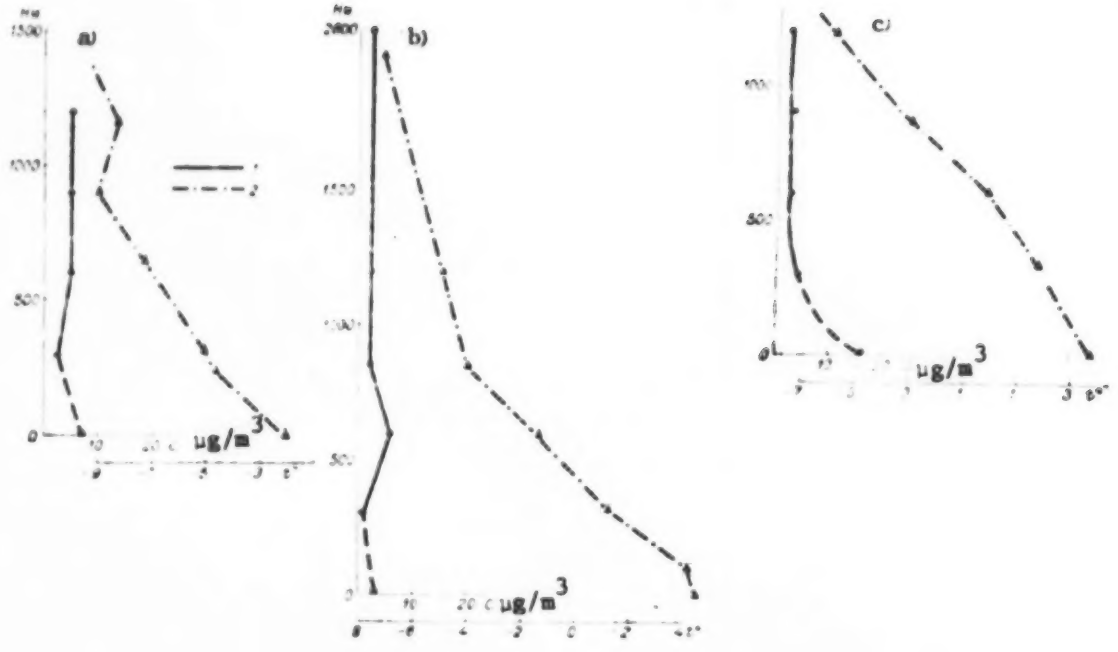

Figure 2. Change in the Concentration of Sulfur Dioxide and Air Temeprature with Altitude under Conditions of Clearly Pronounced Transport of Air Masses in April 1969.

a- 3 April; b- 14 April, 1000; c- 14 April, 2000; 1- Sulfur dioxide; 2- Temperature.

some cases still less). This can be explained by the lack of transport of air masses from the city in the direction of the air field on the days when the observations were made. In only one case on 19 March 1969 (see Figure 1 c) did the concentration of sulfur dioxide at the ground at the air field reach a high value, in excess of 120 micrograms/m^3. In this case, the city was

located in the anterior section of the anticyclone. A north wind was observed at the ground (i.e., from the direction of the city), whose speed reached 10 m/sec. There was a temperature inversion from the ground to the 330 meter level. At this level, the concentration of sulfur dioxide was quite high (approximately 50 micrograms/m^3). However, since the ground concentration of sulfur dioxide was high in this case, regardless of the altitudinal temperature inversion, there was no altitude maximum for the concentration of sulfur dioxide.

The distribution of the sulfur dioxide concentration in the atmosphere with a clearly pronounced transfer of air masses has a completely different nature. Figure 2 shows typical profiles of sulfur dioxide concentration and temperature in the atmosphere for these conditions. On the third of April 1969 (see Figure 2 a) the city was located in an area of directional transfer of air masses from the northwest. The wind speed at the ground was 8 to 10 m/sec. On the 14th of April 1969 (see Figure 2 b, c), the city was in the rear of a cyclone; a southwest wind with a speed of 13 to 18 m/sec. was recorded at the ground.

The high wind speed at the ground and at a high altitude, as well as the developed turbulent exchange, produce a state of equality between the sulfur dioxide concentrations in the atmosphere. In this case, as we can see from the Figures, the concentration of sulfur dioxide at the ground is lower in comparison with the anticyclonic conditions. It changes only slightly with altitude, i.e., there is a nearly uniform distribution of sulfur dioxide in the atmosphere. Even at an altitude of 2600 meters (see Figure 2 b), the sulfur dioxide concentration is not equal to 0, and is almost the same as the values at lower levels.

Hence, the studies that have been carried out have confirmed that there is a constant presence of sulfur dioxide in the atmosphere. The results of the analysis show a marked change in SO_2 content with altitude in the lower layers of the troposphere as a function of the meteorological conditions.

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